

JAPANESE PATENT

96-3-47

PCHe 92-16
JP 4675001

JAPANESE PATENT OFFICE (JP)

PATENT JOURNAL (A)

KOKAI PATENT APPLICATION NO. HEI 4[1992]-75001

Int. cl. ⁵ :	G 02 B 1/04 C 08 F 12/00 220/16
Identification code:	MJT MMC
Sequence Nos. for Office Use:	7132-2K 7211-4J 7242-4J
Application No.:	Hei 2[1990]-188332
Application Date:	July 17, 1990
Publication Date:	March 10, 1992
No. of Inventions:	4 (Total of 8 pages)
Examination Request:	Not requested

PLASTIC LENS

[Puraschick renzu]

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[There are no amendments to this patent.]

Specification

1. Title of the invention

Plastic lens

2. Claims of the invention

1. A plastic lens made from a molding composition containing a hydrogenated polymer produced by hydrogenation of the aromatic ring of an aromatic vinyl monomer, or an aromatic ring of a copolymer made from an aromatic vinyl monomer, and one or more monomers that are copolymerizable with said monomer.

2. The plastic lens specified in claim 1, in which the degree

of hydrogenation of the aromatic ring is 70% or higher.

3. The plastic lens specified in claim 1, in which the plastic lens is a lens for an optical system that utilizes a laser beam as the light source.

4. The plastic lens specified in claim 1, in which the plastic lens is an on-vehicle optical diffusion lens.

3. Detailed explanation of the invention

Industrial application field

The present invention pertains to a plastic lens that can be effectively used as a laser pick-up lens for optical disk readout, camera lenses, and on-vehicle optical diffusion lens, etc. which has a high heat resistance, low moisture absorption, low birefringence, and high weather resistance.

Prior art

In the past, plastic lens have been widely used as lens that do not require high-precision shapes such as eye glasses, magnifiers, and finder lenses for cameras. And the material used for making plastic lens has mainly been polymethylmethacrylate. Polymethylmethacrylate has excellent optical properties, but the moisture absorption is high and heat resistance is low. For this reason, when a plastic is used as the lens material for laser pick-up lenses and camera lens where high performance is required, displacement of the focal point occurs due to moisture, and optical performance is inadequate; furthermore, the maximum

temperature at which the lens can be used is limited, and as suggested in Greis, [Greis et al., SPIE 381, p. 69 (1983)]. As a result, it is not possible to use it as an on-vehicle diffusing lens.

As a result, use of materials such as polycarbonate, poly-4-methyl pentene-1, and polystyrene is conceivable to produce a lens with high heat resistance. However, the birefringence of moldings made of polycarbonate is high and the weather resistance is insufficient; the birefringence of polystyrene is also high, the heat resistance is low, and the weather resistance is also insufficient. As for poly-4-methylpentene-1, the heat resistance is low and the contraction ratio during molding is high, thus, it is not possible to use it for lenses that require a high-precision shape. For the various reasons described above, it is not possible to use the above-mentioned resins for lenses where a high precision shape is required or for on-vehicle diffusing lens.

Also, in addition to the above-mentioned resins, a method where moisture absorption is reduced by use of a copolymer composed of cyclohexylmethacrylate and methylmethacrylate has been suggested (Japanese Kokai Patent Application No. Sho 58[1983]-5318 and Japanese Kokai Patent Application No. Sho 61[1986]-19517), but when said method is used, the heat resistance is low and the mechanical strength is insufficient.

Furthermore, a method in which copolymerization with an N-

substituted maleimide monomer has been suggested in an attempt to increase the heat resistance (Japanese Kokai Patent Application No. Sho 61[1986]-95011), but discoloring takes place during molding, and the light transmittance of the lens becomes poor.

Problems to be solved by the invention

The present invention is based on the background presented above, and the objective of the invention is to produce a plastic lens with well-balanced properties having low moisture absorption, high heat resistance, low birefringence, and high weather resistance.

Means to solve the problem

The inventors discovered that the glass transition temperature of the polymer and the weather resistance can be increased, and furthermore, the birefringence can be decreased when hydrogenation is carried out for the double bonds of an aromatic ring based on a aromatic vinyl monomer included in the polymer and accomplished the present invention.

Thus, the present invention pertains to a plastic lens made of a molding composition containing a hydrogenated polymer produced by hydrogenation of the aromatic ring of an aromatic vinyl monomer or the aromatic ring of a copolymer composed of an aromatic vinyl monomer and one or more monomers that are copolymerizable with said monomer.

When an aromatic vinyl monomer and a copolymer made with

said monomer, and one or more monomers copolymerizable with said monomer of the present invention is used, it is desirable for the mixing ratio of the aromatic vinyl monomer unit to be at least 30 wt%, and when the ratio is less than that, the moisture absorption tends to increase.

Furthermore, it is desirable for the degree of hydrogenation of the aromatic ring to be at least 70%, and when it is less than that, an increase in the birefringence occurs.

For examples of aromatic vinyl monomers that can be used in the present invention, styrenes, α -styrenes such as α -methylstyrene, α -ethylstyrene, α -fluorostyrene, α -chlorostyrene, nuclei-substituted styrenes such as fluorostyrene, chlorostyrene, methylstyrene, butylstyrene, methoxystyrene, hydroxystyrene, carbomethoxystyrene, acetoxystyrene, cyanostyrene, naphthalene derivatives such as α -vinyl naphthalene, β -vinyl naphthalene, α -isopropenyl naphthalene, β -isopropenyl naphthalene, and substitutions thereof, can be mentioned.

For examples of monomers that are copolymerizable with the above-mentioned aromatic vinyl monomers, unsaturated fatty acid esters, vinyl cyanide compounds, unsaturated dibasic acids and derivatives thereof, and unsaturated fatty acids and derivatives thereof can be mentioned.

For examples of unsaturated fatty acid esters, alkylacrylates such as methylacrylate, ethylacrylate, butylacrylate, and 2-ethylhexylacrylate, cycloalkylacrylates such as cyclohexyl acrylate, cyclohexylmethylacrylate, bornylacrylate,

isobornylacrylate, and adamantylacrylate, aromatic acrylates such as phenylacrylate, benzylacrylate, and naphthylacrylate, substituted aromatic acrylates fluorophenylacrylate, chlorophenylacrylate, bromophenylacrylate, fluorobenzylacrylate, chlorobenzylacrylate, and bromobenzylacrylate, alkyl halide acrylates such as fluoromethylacrylate, fluoroethylacrylate, chloroethylacrylate, and bromoethylacrylate, acrylic acid esters such as hydroxyalkylester acrylate, glycidyl acrylate, ethylene glycol acrylate, polyethylene glycol acrylate, alkylaminoalkylester acrylate, and cyanoalkylester acrylate, alkylmethacrylates such as methylmethacrylate, ethylmethacrylate, butylmethacrylate, and 2-ethylhexyl methacrylate, cycloalkylmethacrylates such as cyclohexyl methacrylate, bornylmethacrylate, bornylmethacrylate, and adamantylmethacrylate, aromatic methacrylates such as phenylmethacrylate, benzylmethacrylate, and naphthylmethacrylate, substituted aromatic methacrylates fluorophenylmethacrylate, chlorophenylmethacrylate, bromophenylmethacrylate, fluorobenzylmethacrylate, chlorobenzylmethacrylate, and bromobenzylmethacrylate, alkyl halide methacrylates such as fluoromethylmethacrylate, fluoroethylmethacrylate, chloroethylmethacrylate, and bromoethylmethacrylate, methacrylic acid esters such as hydroxyalkylester methacrylate, glycidyl methacrylate, ethylene glycol methacrylate, polyethylene glycol methacrylate, alkylaminoalkylester methacrylate, and cyanoalkylester methacrylate, α -substituted esters such as α -fluoroacrylate, α -

chloroacrylate, and α -cyanoacrylate, etc. can be mentioned

For examples of vinyl cyanide compounds, acrylnitrile, methacrylnitrile, etc. can be mentioned.

For examples of unsaturated dibasic acids and the derivatives thereof, N-substituted maleimides such as N-methylmaleimide, N-ethylmaleimide, N-propylmaleimide, N-butylmaleimide, N-hexylmaleimide, N-phenylmaleimide, N-methylphenylmaleimide, N-chlorophenylmaleimide, N-methoxyphenylmaleimide, and N-carboxyphenylmaleimide, maleic acid, maleic anhydride, fumaric acid, etc. can be mentioned.

For examples of unsaturated fatty acid and derivatives thereof, (meth)acrylamides such as acrylamide, methacrylamide, N-dimethyl acrylamide, N-diethyl acrylamide, N-dimethyl methacrylamide, and N-diethyl methacrylamide, metal salts of acrylic acid or methacrylic acid such as calcium acrylate, calcium methacrylate, barium acrylate, barium methacrylate, lead acrylate, lead methacrylate, tin acrylate, tin methacrylate, zinc acrylate, and zinc methacrylate, and acrylic acid, methacrylic acid, etc. can be mentioned.

Among the above-mentioned copolymerizable monomers, use of N-substituted maleimide is especially desirable since the material increases the heat resistance.

As for the polymerization reaction method that can be used to produce the above-mentioned polymers, any conventional method such as solid polymerization, suspension polymerization, emulsion polymerization, and solution polymerization, can be used, and

from the standpoint of controlling of the migration of impurities inside the resin at the time of molding and care required in handling, either the solid polymerization or suspension polymerization is desirable.

For examples of polymerization initiators, any conventional polymerization initiator commonly used for standard radical polymerization, for example, organic peroxides such as benzoyl peroxide, lauroyl peroxide, di-t-butyl peroxyhexahydro-terephthalate, t-butylperoxy-2-ethylhexanoate, and 1,1-di-t-butylperoxy-3,3,5-trimethyl cyclohexane, azo compounds such as azobisbutylonitrile, azobis-4-methoxy-2,4-dimethylvaleronitrile, azobiscyclohexanone-1-carbonitrile, and azodibenzoyl, water-soluble catalysts such as potassium persulfate and ammonium persulfate, redox catalysts consisting of a combination of a peroxide or persulfate and a reducing agent, etc. can be mentioned. It is desirable to use the above-mentioned polymerization initiator in the range of 0.01-10 wt% for the total amount of the monomer. Furthermore, in order to adjust the molecular weight, a mercaptan type compound, thioglycol, carbon tetrabromide, α -methylstyrene dimer, etc. can be used for polymerization modifiers, as needed.

It is desirable to select the polymerization temperature in the range of 0-200°C, but 50-120°C is especially suitable.

For solvents used in solution polymerization, for example, benzene, toluene, xylene, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, dichloroethylene, etc. can

be used.

Suspension polymerization is carried out in an aqueous medium, and suspension agents and suspension coagents are added, as needed. For examples of suspension agents, water-soluble polymers such as polyvinyl alcohol, methylcellulose, and polyacrylamide, slightly soluble inorganic materials such as calcium phosphate and magnesium pyrophosphate, etc. can be used, and the amount of water-soluble polymer used is preferably in the range of 0.03~1 wt% for the total amount of the monomer, and the amount of the slightly soluble inorganic material used is preferably in the range of 0.05~0.5 wt% for the total amount of monomer.

For examples of suspension coagents, anionic surfactants such as dodecylbenzene sodium sulfonate can be mentioned, and when a slightly-soluble inorganic material is used as a suspension agent, it is desirable to use a suspension coagent in combination. The amount of the suspension coagent is preferably used in the range of 0.001~0.02 wt% for the total amount of monomer.

The molecular weight of the polymer produced as described above is not especially limited, but from the standpoint of moldability, heat resistance, mechanical strength, etc. those with a weight average molecular weight in the range of 10,000~1,000,000 (when the measurement is made using the calibration curve of polystyrene reference material by gel-permeation chromatography), are desirable.

Hydrogenation of the aromatic ring in the polymer is carried out in a solution in the presence of a hydrogenation catalyst in the usual manner. For the hydrogenation reaction solvent, it is desirable to select a solvent that is inert with respect to the hydrogenation reaction, and in specific terms, ethers such as tetrahydrofuran and dioxane, alicyclic hydrocarbons such as cyclohexane and methyl cyclohexane, esters, etc. can be mentioned. From the standpoint of reactivity and handling, etc., it is desirable to dissolve an aromatic vinyl monomer in the above-mentioned solvent at a concentration of 2~50 wt% and the hydrogenation reaction is carried out.

For the hydrogenation catalyst, one with a high catalytic activity and catalytic selectivity is desirable to control the side reactions that rupture the molecular chain of the polymer that is being hydrogenated, and in specific terms, precious metals such as ruthenium, rhodium, palladium, platinum, and nickel, and oxides, salts, and complexes thereof, or catalysts produced by depositing the above-mentioned precious metals on a material such as activated carbon, diatomaceous earth, alumina, etc. can be mentioned. Among those listed above, Raney nickel, Raney cobalt, stabilized nickel, stabilized ruthenium, and stabilized rhodium deposited on an activated carbon and alumina carrier is especially suitable from the standpoint of reactivity, etc. For the amount of the above-mentioned precious metals deposited on the carrier, 0.1~25 wt% is desirable. Also, it is desirable to use the hydrogenation catalyst in a range of 5~50

wt% for the aromatic vinyl monomer unit.

The conditions used for the hydrogenation reaction are appropriately determined according to the type and concentration of the aromatic vinyl monomer used, and the type of solvent, and the type and the concentration of the catalyst used, but in general, the reaction is carried out under a pressure of 20~250 kgf/cm², and a reaction temperature of 50~240°C.

It is desirable for the degree of hydrogenation of the aromatic ring to be at least 70%, and at least 80% is preferable, but at least 95% is ideal. The degree of hydrogenation of 100% can be achieved by adjusting the hydrogenation reaction conditions. The degree of hydrogenation can be easily determined by measurement of spectra by methods such as NMR and IR.

The molecular weight of the polymer produced by the hydrogenation reaction varies depending on the molecular weight of the aromatic vinyl monomer before the hydrogenation reaction, the reaction temperature, and the type of catalyst used, but from the standpoint of the moldability and heat resistance, a weight average molecular weight (in terms of polystyrene) in the range of 50,000~1,000,000 is desirable.

Other polymers, thermal-degradation resisting compounds such as phenols, phosphites, and thioethers to prevent thermal degradation, release agents such as aliphatic alcohols, aliphatic esters, and fluorine-type surfactants, and other additives such as lubricants, ultraviolet absorbers, and antistatic agents, etc. also can be added to the hydrogenated polymer produced above, as

needed.

As a means to produce a plastic lens from the molding composition that includes the above-mentioned hydrogenated polymers, conventional injection molding, compression molding, extrusion molding, casting, etc. can be used.

The plastic lens of the present invention can be effectively used for optical system lens used for laser beams, on-vehicle light-diffusion lens used for head lamps, etc., video camera lenses, standard camera lenses, telescope lenses, etc. In particular, the plastic lens of the present invention is suitable for the condenser lens and objective lens for laser beams used for optical disks because of the low moisture absorption and low birefringence of the hydrogenated polymer, and for lenses used for head lamps because of the good weather resistance and heat resistance. Furthermore, it can be effectively used for prism as well.

Furthermore, inorganic compounds, organic silicon compounds, acrylic polymers, fluoro-resins, etc. can be coated onto the surface of the plastic lens of the present invention using conventional methods such as heat curing, ultraviolet curing, vacuum deposition, sputtering, and ion plating, etc. so as to further improve properties such as heat resistance, optical properties, and abrasion reaction.

Application Examples

In the following, the present invention is further explained

in specific terms, but the present invention is not limited to these application examples.

Application Example 1

Synthesis of an aromatic vinyl polymer

Using 42 g of a 10 wt% aqueous suspension of basic calcium phosphate as a dispersant, 0.004 g of dodecylbenzene sodium sulfonate and 2400 g of purified water were poured into a 5 l separation flask, stirring was provided and a suspension was produced. The component shown below was added to the above-mentioned mixture, and a polymerization reaction was carried out in a nitrogen atmosphere at 85°C for 6 hours at a mixing speed of 260 rpms, and a polymerization reaction was further carried out at 98°C for 3 hours, and a polymer particles were produced.

Styrene	100 parts by weight
Benzoyl peroxide	1.2 parts by weight

The polymer particles produced were then washed in an acid, rinsed in water, and dehydration and drying was performed. When the molecular weight of the above-mentioned polymer particles were measured by gel-permeation chromatography (GPC), the weight average molecular weight was 32×10^4 (in terms of polystyrene).

Synthesis of hydrogenation polymer

100 parts by weight of the above-mentioned dried polymer was dissolved in 1000 parts by weight of cyclohexane, 15 parts by

weight of stabilized Ni (deposited on an activated carbon carrier, deposition ratio of 10 wt%), and 20 parts by weight of isopropenyl alcohol were added to the above solution and mixing was performed; it was then placed in an autoclave. Subsequently, the atmosphere inside the autoclave was purged with nitrogen gas, and stirring was performed at a speed of 900 rpm, and the temperature was increased to 180°C. After the temperature was increased, hydrogen gas was supplied from an automatic pressure controller at a rate of 100 kg/cm³, and a hydrogenation reaction was carried out for 8 hours. After cooling, 1000 parts by weight of cyclohexane was added to dilute, filtration was performed using a centrifuge, and the Ni catalyst and insoluble components were removed. After filtration, the solution was poured into 20,000 parts by weight of methanol, and the hydrogenated polymer was precipitated and separated from the solution, and vacuum drying was performed. When the molecular weight of the hydrogenated polymer was measured after the vacuum drying using the GPC method, the weight average molecular weight was 12×10^4 (in terms of polystyrene). Furthermore, when the degree of hydrogenation was calculated based on the absorption peak in the infrared absorption spectra near 900 cm⁻¹, the degree of hydrogenation was found to be 100%. The infrared absorption spectrum of the polymer before hydrogenation and after hydrogenation are shown in Fig. 1 and Fig. 2, respectively. The above-mentioned hydrogenation polymer was molded to form a sheet with dimensions of 40 x 50 x 3 (mm) at a resin temperature of

240°C using an injection molding machine, and measurements were made of the moisture absorptivity and other properties. The results obtained are shown in Table I.

It should be noted that the moisture absorptivity was obtained by first drying the molding with dimensions of 40 x 50 x 3 (mm), measuring the dry weight, then, measuring the weight after storing the sample at a temperature of 80°C and a relative humidity of 95% for 240 hours; the calculation was made using the mathematical equation shown below.

$$\text{Moisture absorptivity (\%)} = \frac{[(\text{wet weight}) - (\text{dry weight})]}{\text{dry weight}} \times 100 (\%)$$

The glass transition temperature was measured by means of differential scanning calorimetry (DSC), and the temperature at which the transition begins to occur was defined as the glass transition temperature.

For the birefringence, the center point of the molding was measured by the elipsometric method.

For the light transmittance, the transmittance at a wavelength of 540 nm was measured using a spectrophotometer.

Furthermore, UV exposure was carried out for 1000 hours at 63°C using an ultraviolet fadeometer (UV, diameter of the carbon carrier 50 mm), and the total light transmittance was measured after the exposure test.

The refractive index and Abbe number were measured using an Abbe refractometer.

Furthermore, injection molding was carried out for a hydrogenation polymer produced separately at a resin temperature of 240°C, and a lens with the shape shown in Fig. 3 was produced.

The above-mentioned lens was stored at a temperature of 60°C and a relative humidity of 95% so as to absorb the moisture, and the moisture absorption ratio and the variation in the wavefront aberration was measured. The results obtained are shown in Fig. 4.

Application Examples 2, 3, and 4

The monomer components shown in Table I were used, and synthesis of a polymer, hydrogenation, and measurement of the resulting properties was performed as in Application Example 1 above. The results obtained are shown in Table I.

Comparative Example 1

A commercial polystyrene (product of Mitsubishi Monsanto Chemical Corp. (Ltd.), Dialex [phonetic] HH-102) was used, and injection molding was used to produce a flat sheet with dimensions of 40 x 50 x 3 (mm), and the properties were measured. The results obtained are shown in Table I.

Comparative Example 2

A commercial polycarbonate (product of Teijin Chemical Corp. (Ltd.), Panlite [phonetic] AD-5503) was used, and injection molding was used to produce a flat sheet with dimensions of 40 x

50 x 3 (mm), and the properties were measured. The results obtained are shown in Table I.

Comparative Example 3

A commercial polymethylmethacrylate (product of Mitsubishi Rayon Corp. (Ltd.), Acrypet [phonetic] VH-001) was used, and injection molding was used to produce a flat sheet with dimensions of 40 x 50 x 3 (mm), and the properties were measured. The results obtained are shown in Table I. Furthermore, a lens with the shape shown in Fig. 4 was produced by injection molding at a resin temperature of 240°C. The above-mentioned lens was stored at a temperature of 70°C and a relative humidity of 85% so as to absorb the moisture, and the moisture absorption ratio and variation in the wavefront aberration were measured. The results obtained are shown in Fig. 5.

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Table I

			Application Examples				Comparative Examples		
			1	2	3	4	1	2	3
Monomer component	(parts by weight)	Styrene	100	70	70	—			
		α -methyl styrene	—	—	—	54			
		Methylmet hacrylate	—	30	20	46			
		Cyclohexyl maleimide	—	—	10	—			
Properties	Degree of hydrogenation (%)		100	97	96	96	—	—	—
	Moisture absorption ratio (%)		0.1	0.6	0.4	0.8	0.1	0.4	2.2
	Light transmittance (%)		91	92	92	91	89	90	93
	Refractive index (nd)		1.514	1.507	1.509	1.506	1.598	1.596	1.490
	Abbe number (vd)		55	56	56	54	32	33	57
	Birefringence (nm)		15	18	12	20	400 or higher	160	20
	Glass transition temperature (°C)		130	123	129	130	100	130	105
	Light transmittance after ultraviolet exposure (%)		90	91	92	90	81	84	92

Effect of the invention

The plastic lens of the present invention exhibits a low moisture absorption, and the variation in shape of the lens when moisture absorption occurs is low; as a result, variation in the wavefront aberration is low, and it can be used effectively as a lens where high precision is required.

Furthermore, the birefringence of the above-mentioned lens

is low; thus, it can be effectively used as an optical system lens where a laser beam is used as the light source such as the laser pick-up lens where an optical distortion near zero is required.

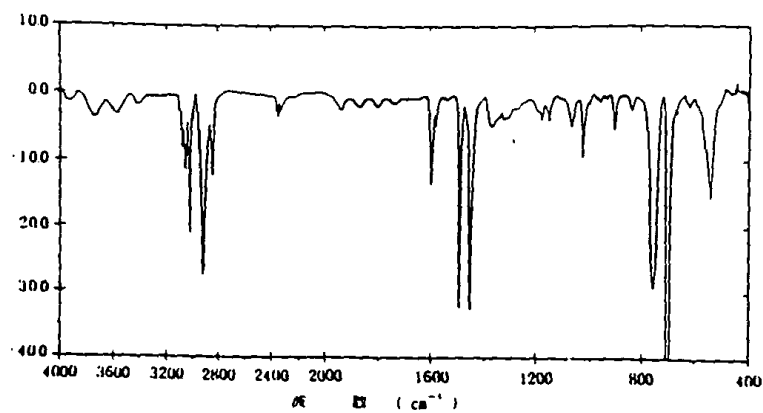
In addition, the plastic lens of the present invention has a high heat resistance as well as good weather resistance; thus, it can be used as a diffusing lens on vehicles for purposes such as headlight lenses.

4. Brief explanation of the figures

Fig. 1 shows the infrared absorption spectrum of the polystyrene produced in Application Example 1. Fig. 2 shows the infrared absorption spectrum of the hydrogenated polymer produced in Application Example 1. Fig. 3 shows a cross-section view of the lens produced in Application Example 1. Fig. 4 is a graph that shows the relationship between moisture absorption and wavefront aberration of the lens produced in Application Example 1. Fig. 5 is a graph that shows the relationship between the moisture absorption and wavefront aberration of the lens produced in Comparative Example 3.

Agent: Kunihiro Wakabayashi, patent attorney

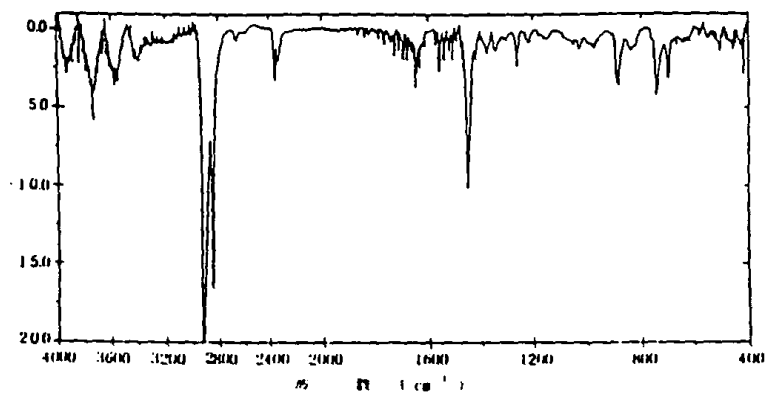
[Fig. 1]



Vertical axis: Transmittance (relative %)

Horizontal axis: Wave number (cm⁻¹)

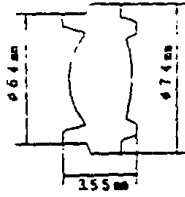
[Fig. 2]



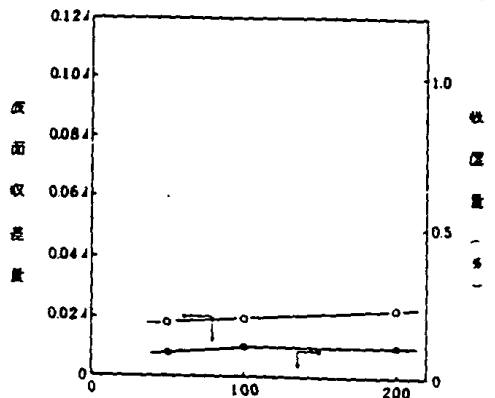
Vertical axis: Transmittance (relative %)

Horizontal axis: Wave number (cm⁻¹)

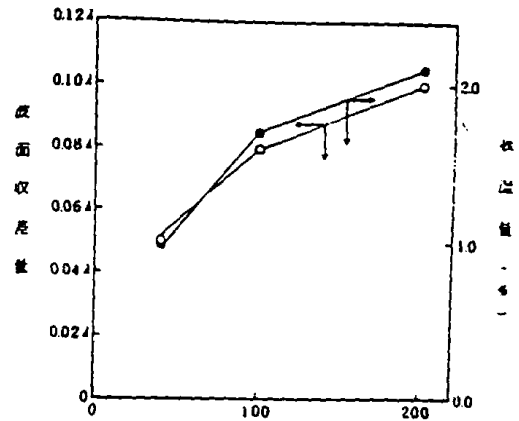
[Fig. 3]



[Fig. 4]



[Fig. 5]



Vertical axis:

Left side: Wavefront aberration

Right side: Moisture absorption (%)

Horizontal axis: Storage time (hr)